Low-Temperature Magnetic Spectroscopy of a Dilute Magnetic Semiconductor

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A newly developed integrated SQUID magnetic spectrometer yields direct high-resolution measurements of the optically induced magnetization in a 10-μm-diam sample of $Cd_{0.8}Mn_{0.2}Te$. Both the magnitude and the picosecond dynamics of the magnetic response have been studied and are seen to be dramatically dependent on the energy and polarization of the optical excitation. The data show that the overall sample magnetization changes upon illumination, and that the perturbed spins equilibrate through spin-lattice relaxation.

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Magnetic and diluted magnetic semiconductors (DMS) have enjoyed continued interest and examination, principally because free carriers introduced either by doping[1] or by optical excitation across the band gap[2] couple strongly with the spins in the lattice. In metals, changes in carrier densities ordinarily do not lead to a modification of the magnetic behavior. In magnetic semiconductors, however, carriers may have a profound effect on the magnetic behavior, in some cases reversing the sign of the effective exchange interaction between ion spins.[1,3] These interactions also affect the energetics of the carriers, leading to anomalously large spin splittings of the conduction and valence bands as well as magnetization-dependent exciton recombination and polarization effects. Recent time-resolved experiments[4-6] in Mn-based II-VI DMS have succeeded in probing some of the dynamical aspects of these phenomena. However, the fundamental spin mechanics in these systems are still not well understood. In order to obtain a detailed understanding of the static and dynamic magnetic properties of DMS, we have developed a method of observing photoinduced magnetization[7] in real time with picosecond resolution.

In this Letter we describe the new static and picosecond time-resolved techniques used to obtain absolute measurements of the magnetic response of a material upon optical stimulation. These methods offer a high-resolution magnetic spectroscopy which is useful for any system in which optical excitations are capable of perturbing the magnetic state. The photon energy and polarization as well as the sample temperature may be changed in order to explore the energetics and the orientation of the induced magnetization and its thermal dependence. Moreover, the fast time resolution allows the dynamical aspects of the system to be studied in different regimes as the optical energy and intensity are varied, providing information on the microscopic aspects of the induced magnetism and its subsequent relaxation. Although the construction details of the spectrometer are provided elsewhere,[8] a brief description of the apparatus will be given here. A planar thin-film dc SQUID[9] operating at cryogenic temperatures serves as a detector measuring directly the absolute change in magnetization of a small 10-μm-diam sample. In the present SQUID design the magnetic flux is sensed by two square pickup coils 17.5 μm on the diagonal wound in opposite senses to eliminate stray magnetic fields. The sample fits into a 10-μm depression in one of the loops, although larger samples are easily accommodated by placing them over only one of the planar pickup loops. The sensitivity of the SQUID used for these experiments is limited by flux noise and found to be $3\times10^{-6}\phi_0$ at dc, where ϕ_0 is the flux quantum, 2.07×10^{-7} G cm^2.

The optical configuration relies on the ultrashort light pulses from a synchronously pumped dye laser, producing a train of energy-tunable pulses of 4-psec duration at a 76-MHz repetition rate. The train of linearly polarized pulses is split into pump and probe beams of intensity ratio 10:1 and converted to circularly polarized light with a quarter-wave plate, then recombined and conducted to the sample at cryogenic temperature through a polarization-preserving optical fiber. Static spectroscopy data are collected by our tuning the laser while chopping the excitation beam at 197 Hz and lock-in detecting the resulting SQUID signal. Time-resolved data involve tuning of the laser to a fixed energy and chopping of the probe beam which is systematically delayed from the excitation pulse by a computer-driven delay line. Thus at any particular instant in delay time the probe beam measures the magneto-optical susceptibility χ_{op} by inducing a magnetization $\delta M = \chi_{op}\delta I$, where δI is the probe intensity. Time-resolved measurements require greater sophistication in that the signal extracted from the SQUID is the signal-averaged response to the weak probe optical excitation. The probe pulses arrive at regular time intervals after the pump pulse has perturbed the system. By varying the relative excitation-probe delay time, this "optical boxcar" technique then measures the time-dependent variation in the optical susceptibility which has been introduced by the pump. As the time-resolved signal is derived from the differences of the probe-induced response with and without the pump excitation, the observed signal measures solely the effect of the pump pulse. Therefore, although the weak probe pulse

itself causes a change in magnetization which is unrelated to the pump pulses, the measurement technique is independent of probe energy.

We have investigated the static and dynamic magnetic response of a small, $\sim 10\times 10\times 1$ μm^3, single-crystal platelet of $Cd_{0.8}Mn_{0.2}Te$ to optical excitations spanning the energy range from below the bound magnetic polaron (BMP)[10] to energies 100 meV greater than the band gap. The sample composition and band gap[11] were estimated from microprobe analysis in conjunction with low-field rf SQUID magnetic-susceptibility data and Gandolfi camera measurements. We chose this particular paramagnetic material since it is a well-characterized cubic semiconductor, relatively easy to fabricate and its optical properties have been studied extensively in the band-edge region. Furthermore, the band-gap energy is such that the dynamical processes of the system can easily be probed at energies both above and below the gap.

The results of the static magnetic spectroscopy are summarized in Fig. 1 which shows the magnetic response to optical excitation at constant intensity from 1.83 to 2.0 eV at two temperatures. The light is circularly polarized and incident in the direction normal to the plane of the SQUID pickup loop. Three regions in excitation energy are clearly defined in these spectra. Well below the band edge, the induced magnetism is essentially negligible as is expected, since the sample is relatively transparent at this wavelength. In the region just below the band edge, the signal changes rapidly, reaching a pronounced maximum, then decreasing with increasing laser energy. Finally, at energies above the gap, the response is constant. We also note that the signal is sensitive to temperature, decreasing noticeably when the sample is warmed to 5.8 K. Several important conclusions may be drawn directly from these curves. It is clear that the magnetization of the sample changes when illuminated with light of sufficient energy, since the entire sample is in the SQUID loop. Furthermore, if the quantum efficiency is assumed to be constant, the induced magnetization per incident photon is independent of energy for excitation well above the gap, but increases rapidly near the band edge. This implies that there is a spin-alignment mechanism only important when the pumping is near the band edge, which we attribute to magnetic polaron formation. A localized electron or hole tends to organize ferromagnetically the spins of the magnetic ions in its neighborhood through the strong coupling between carrier and ion spins. The resulting magnetic polaron thus has an effective moment which is much larger than that of a single ion. For excitation with circularly polarized light at an energy slightly below the gap, it has been shown that a considerable spin polarization of the magnetic polarons can be achieved.[12] Thus the peak in the magnetic response is due to the creation of magnetic polarons whose large magnetic moments are oriented perpendicular to the SQUID loop. It is important to note that the signal in this case is due to the magnetic ions which align themselves in the strong exchange field of the localized carrier. This process is described by a spin-lattice relaxation of the ions in the effective field associated with the diagonal part of the exchange interaction, Js_zS_z in the standard notation. As a result the overall magnetization of the sample increases. This process is distinct from the spin-flip scattering events which proceed through the nondiagonal parts of the spin interaction,[7] Js_+S_- and Js_-S_+. For excitation with light at higher energies, this spin-flip exchange scattering transfers the carrier spin polarization to the Mn ions resulting in the observed energy-independent magnetization. Although polarons will still form when the carriers are eventually trapped, they will not contribute to the net magnetization because of their random orientation.

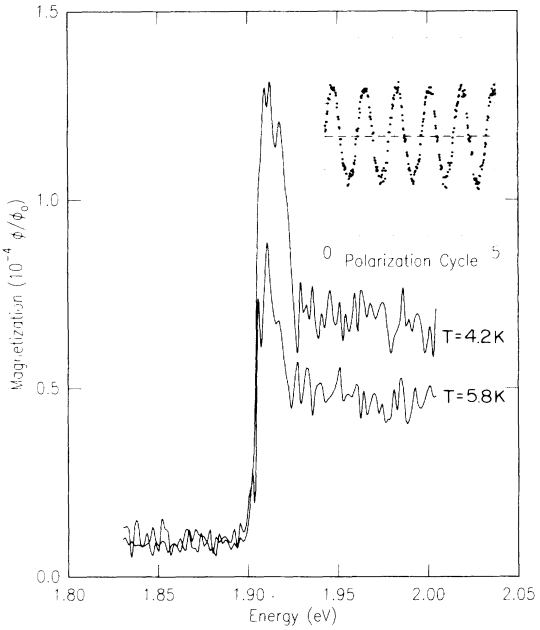

FIG. 1. Magnetic spectroscopy of a 10-μm-diam sample at two temperatures, illuminated with a constant laser intensity of 5 mW. Inset: The induced magnetization as a function of photon polarization at $E=1.915$ eV, where each polarization cycle is 0 to 180 degrees. The polarization was modulated at 197 Hz and the signal was averaged for 30 min.

When the pumping is with linearly polarized light, the average photon angular momentum is zero, and no induced moment is observed in the sample. A dramatic demonstration of the polarization dependence of the signal is given in the inset of Fig. 1. In this case the incident energy is tuned to the maximum signal and the polarization is modulated from σ_+ to σ_- for several cycles. The results show that the direction of the induced magnetization is determined by the orientation of the photoexcited spin-polarized carriers. Clearly heating, which is independent of polarization vector, does not contribute to the photoinduced signal.

The magnitude of the observed magnetization also deserves comment. The sensitivity of the present measurements may best be described by an estimate of the total number of aligned Mn spins necessary to produce the maximum signal of $\sim 1.4\times10^{-4}\phi_0$. This is done by our calculating the equivalent magnetization by use of the SQUID calibration data of Ketchen, Kopley, and Ling,[9] who find that a 5×10^{-4}-cm-diam sphere of Sn in an external field $H=5$ Oe excludes $0.7\phi_0$ units of flux in cooling through the superconducting transition temperature. Thus ϕ_0 is equivalent to $3\times H\times V_{sp}/8\pi\times0.7=5.58\times10^{-11}$ emu and the number of Mn spins, N_{Mn}, is obtained by expressing the observed signal in terms of the equivalent magnetization, i.e.,

$$N_{Mn}Jg\mu_B = 1.4\times10^{-4}\times5.58\times10^{-11}=7.8\times10^{-15}, \quad (1)$$

where μ_B is the Bohr magneton, and with $J=\frac{5}{2}$, and $g=2$ for Mn^{+2} ions, or $N_{Mn}=1.7\times10^5$ spins. The significance of this result may be put into perspective by recalling that magnetic-resonance spectrometers generally require 10^{13} spins to obtain usable signals. We may, furthermore demonstrate that 1.7×10^5 spins is reasonable by estimating the number of oriented polarons, N_p, formed during excitation with polarized photons. It is known that the luminescence efficiency for $Cd_{1-x}Mn_xTe$ quantum wells is at least 100 times greater than that from bulk $Cd_{1-x}Mn_xTe$.[12] Therefore, 0.01 represents an estimate of the quantum efficiency for the production of polarons. In addition, it is known that the net polaron polarization[13] is 0.17. Thus

$$N_p=0.01\times0.17\times P\times\tau\times E^{-1}\simeq1.9\times10^4, \quad (2)$$

where P, the incident power, is 5 mW, $\tau\simeq7\times10^{-10}$ sec is the polaron lifetime,[6] and $E\simeq1.91$ eV. On the assumption that the polaron contains roughly 25 fully aligned Mn ions,[14] the number of oriented Mn spins is $\sim5\times10^5$, consistent with the number actually observed. It is worthwhile noting that, since the sample contains about 3×10^{11} spins, on the average only one spin in a million is polarized.

The dynamic magnetic response of the sample is found to be critically dependent on the energy of excitation. The transient magnetization induced by the pump pulse is observed through its effect on $dM/dI=\chi_{op}$ as measured by the probe pulse, thereby monitoring relative changes in magnetization as a function of delay time. The picosecond variation of magnetization with time for the three regions of energy is given in Fig. 2. Curve *a*, with the exception of the anomaly indicative of the pump pulse, is featureless as expected for excitation energies well below the band gap. Since no electron-hole pairs are created, no magnetic response ensues. Curves *b* and *c*, on the other hand, exhibit dramatically different time dependencies. At $e=1.915$ eV, where the response is due to the creation of oriented magnetic polarons, the

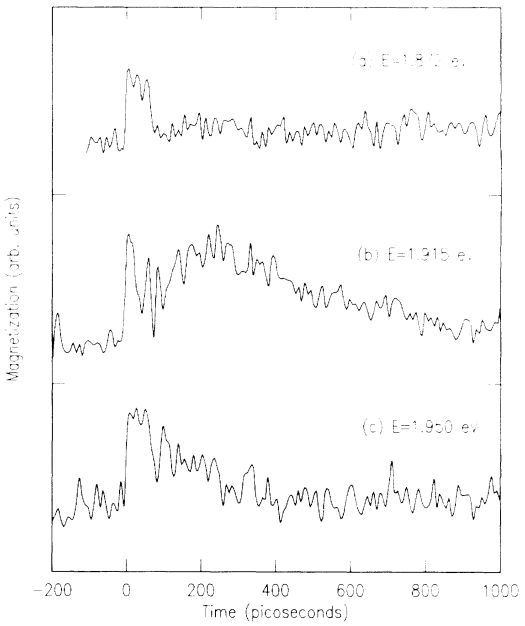

FIG. 2. Picosecond time-resolved magnetization for $Cd_{0.8}Mn_{0.2}Te$ at three different excitation energies including curve *a*, well below the band-gap energy; curve *b*, at the polaron-formation energy; and curve *c*, above the band gap. The relative vertical displacements are arbitrary.

magnetization rises from zero and peaks after ~250 psec, then decays after ~1000 psec. At higher energies, $e=1.95$ eV, the initial response is instantaneous within the 2-psec resolution and the magnetization decays after approximately 300 psec, much more quickly than at lower energy.

Focusing first on the 1.915-eV data, it should be noted that the initial rise time of about 250 psec is consistent with the polaron formation time observed through time-resolved Faraday rotation.[5] In addition, the data are consistent with several nonmagnetic measurements of this time,[4,6] in which the time evolution of the polaron binding energy was monitored. This strengthens our conclusion that we are directly witnessing the dynamics of the local spin organization as the polaron is formed. The long ~1000-psec decay is consistent with the carrier recombination in this material.[6] The magnetic spins are kept aligned by the strong exchange field provided by the localized carriers, until the electrons and holes recombine and the magnetic spins relax to random orientations. Thus the dynamic data at this energy provide a complete description of the polaron formation and subsequent decay as measured through its magnetic properties.

When the pumping is at $E=1.95$ eV, the increase in magnetization is almost instantaneous. The excited, polarized carriers transfer their polarization rapidly through spin-flip scattering via the Mn exchange interaction, a process which has been calculated[7] to occur on a

time scale of ~1 psec for nearly free carriers. We observe the small, relatively uniform magnetization which is induced initially as a result of the spin-flip scattering. This magnetization relaxes through the spin-lattice interaction. Therefore, we deduce that the spin-lattice relaxation time is about 300 psec in this material.

Several remarks should be made concerning this spin relaxation time. The time is much shorter than the 10–100 msec measured in extremely dilute magnetic systems.[15] Since the magnetization of the entire sample changes, spin-diffusion processes cannot account for the observed time scale. Furthermore, the relaxation rate is independent of the field on the ion as evidenced by the fact that the same (~300 psec) time scale is observed in the formation of the polaron, where the ion relaxes in a strong exchange field. Similar times are also measured in the presence of an external field.[5] Finally, the temperature dependence of the signal indicates that the relaxation time decreases as the temperature is raised.[7] All of the above observations can be explained in terms of the spin mechanics of clusters of Mn ions coupled through the antiferromagnetic Mn-Mn exchange interaction. If we assume a random distribution of magnetic ions, there will be many clusters of various shapes and sizes. For one of the spins in such a group, the total exchange field will be anisotropic, allowing an efficient spin coupling to the lattice.[16] Similar mechanisms have been observed in other systems[17] where, at relatively modest concentrations of the magnetic species (< 10%), the relaxation rates have been increased by 4 orders of magnitude over the single-ion rate. To estimate a time scale for the spin relaxation of a large cluster we use an expression for the first-order, one-photon spin-transition rate,[16]

$$1/\tau \simeq [\delta^3 (2J_1')^2/\pi\rho\hbar^4 v_t^5]\coth(\delta/2KT). \quad (3)$$

Here δ is the exchange energy of the spin which we shall take as $2.4\times 2J_1$, where 2.4 is the average number of magnetic nearest neighbors for a given ion, and $2J_1 = 1.2$ meV is the spin-exchange coupling constant in the standard notation. The density, ρ, is 5.85 g/cm^3, the transverse sound velocity, v_t, is 1.85×10^5 cm/sec, and $2J_1' = 13.4$ meV is the change in $2J_1$ per unit strain.[18] Using these parameters, we calculate $\tau \sim 120$ psec, consistent with the time observed.

In conclusion, we have studied the details of photo-induced magnetization in $Cd_{0.8}Mn_{0.2}Te$ with use of a dc SQUID-based magnetic spectrometer to probe the magneto-optical properties over a broad range of photon energy and polarization. This technique allowed us to study the induced magnetism from dc to picosecond time scales, revealing the strong dependence on excitation energy of both the magnitude and the temporal characteristics of the response. By variation of the energy, different spin alignment and relaxation processes were then investigated separately, providing a new understanding of the spin mechanics in diluted magnetic semiconductors.

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